

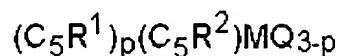
Claims

- [1] 1. A supported hybrid metallocene catalyst with at least two different metallocene compounds supported on a single support, wherein:
at least one metallocene compound is supported on the support by a chemical bond of its ligand to the support surface; and
the other metallocene compound is supported on the support by a chemical bond of its ligand to a cocatalyst chemically bonded to the support surface.
2. The supported hybrid metallocene catalyst according to Claim 1, wherein said at least one metallocene compound is a catalyst for preparing low molecular weight polyolefin and the other is a catalyst for preparing high molecular weight polyolefin.
3. The supported hybrid metallocene catalyst according to Claim 2, wherein the low molecular weight polyolefin has a molecular weight ranging from 1,000 to 100,000, and the high molecular weight polyolefin has a molecular weight higher than that of the low molecular weight polyolefin, ranging from 10,000 to 1,000,000.
4. The supported hybrid metallocene catalyst according to Claim 1, wherein the supporting amount of the metallocene compounds is 0.1 to 20 wt% of the total supported hybrid metallocene catalyst weight, based on the weight of metals comprised in each metallocene compound.
5. The supported hybrid metallocene catalyst according to Claim 1, wherein the supporting amount of said at least one metallocene compound is 0.01 to 100 mol for 1 mol of the other metallocene compound.
6. The supported hybrid metallocene catalyst according to Claim 1, wherein the supported hybrid metallocene catalyst is further supported 1 to 10,000 mol of a cocatalyst component for polyolefin polymerization per 1 mol of metals comprised in the metallocene compound, based on the metal contained in the cocatalyst.
7. A supported hybrid metallocene catalyst for preparing polyolefin having a bimodal or broad molecular weight distribution, which comprises:
a) a catalyst component comprising:
i) a first metallocene compound having an acetal, ketal, tertiary alkoxyalkyl, benzyloxyalkyl, substituted benzyloxyalkyl, monothioacetal or monothioketal group;

- ii) a second metallocene compound having a bridge linkage containing a Lewis base in cyclopentadiene, a cyclopentadiene derivative or a bridge group; and
- iii) an organometallic compound containing a group XIII metal; and
- b) a support having siloxane groups on the surface, on which the catalyst component is supported.

8. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the first metallocene compound is a compound represented by the following Chemical Formula 1:

Chemical Formula 1



wherein:

M is a group IV transition metal;

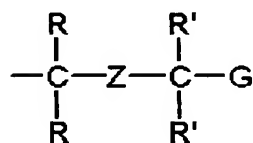
each of (C_5R^1) and (C_5R^2) is cyclopentadienyl which is a metallocene of a group XIV metal substituted by identical or different hydrogen radical, C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl, arylalkenyl radical or hydrocarbyl; cyclopentadienyl wherein two neighboring carbon atoms of C_5 are connected by a hydrocarbyl radical to form one or more C_4 to C_{16} rings; or a substituted cyclopentadienyl ligand;

Q is a halogen radical; a C_1 to C_{20} alkyl radical, alkenyl radical, aryl radical, alkylaryl radical, arylalkyl radical; or a C_1 to C_{20} alkylidene radical;

P is 0 or 1; and

at least one hydrogen radical in R^1 and R^2 is substituted by a radical represented by the following Chemical Formula a, a radical represented by the following Chemical Formula b, or a radical represented by the following Chemical Formula c:

Chemical Formula a



wherein:

Z is an oxygen atom or a sulfur atom;

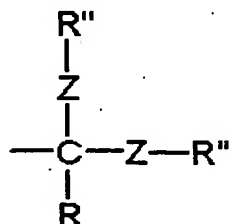
each of R and R' is identical or different hydrogen radical; C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl; or arylalkenyl radical; and the two R's may be connected to form a ring;

G is a C₁ to C₄₀ alkoxy, aryloxy, alkylthio, arylthio, phenyl or substituted phenyl, and may be connected to R' to form a ring;

if Z is a sulfur atom, G should be alkoxy or aryloxy; and

if G is alkylthio, arylthio, phenyl or substituted phenyl, Z should be an oxygen atom;

Chemical Formula b



wherein

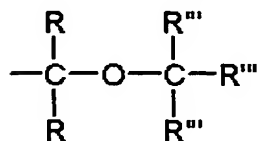
Z is an oxygen atom or a sulfur atom, and at least one of the two Zs is an oxygen atom;

each of R and R'' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

R and R'' may be connected to form a ring; and

unless both R''s are hydrogen radicals, they may be connected to form a ring; and

Chemical Formula c



wherein:

each of R and R''' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

two neighboring R'''s may be connected to form a ring; and

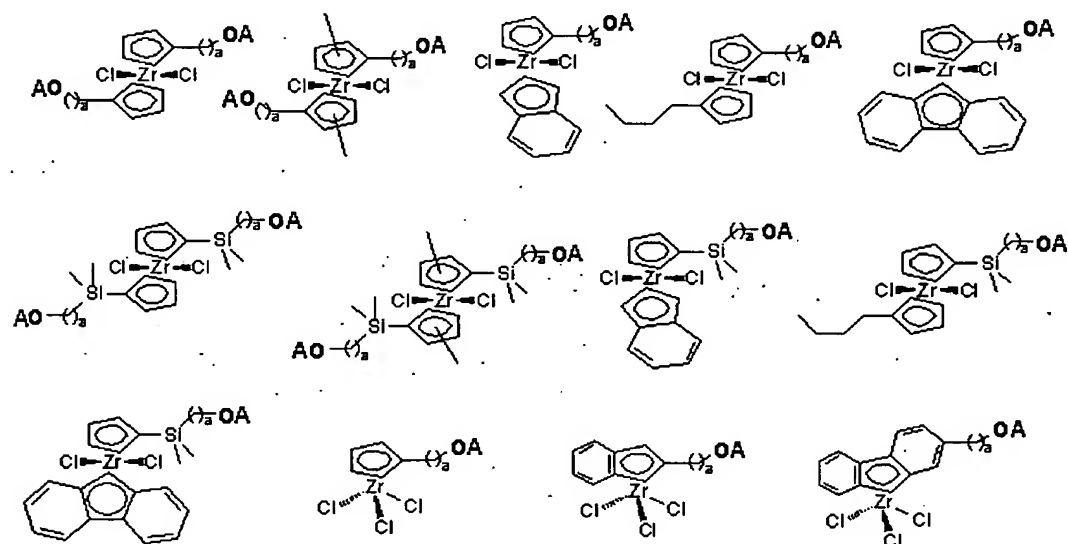
if at least one of Rs is a hydrogen radical, all R'''s are not hydrogen radicals, and

if at least one of R'''s is a hydrogen radical, all Rs are not hydrogen radical.

9. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the first metallocene compound is $[\text{A}-\text{O}-(\text{CH}_2)_2-\text{C}(\text{H})_5-\text{C}(\text{H})_4-\text{ZrCl}_2]$ or $[\text{A}-\text{O}-(\text{CH}_2)_2-\text{C}(\text{H})_9-\text{C}(\text{H})_6-\text{ZrCl}_3]$ (wherein each a is an integer of 4 to 8, and each A is methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranlyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl).

10. The supported hybrid metallocene catalyst for preparing polyolefin according

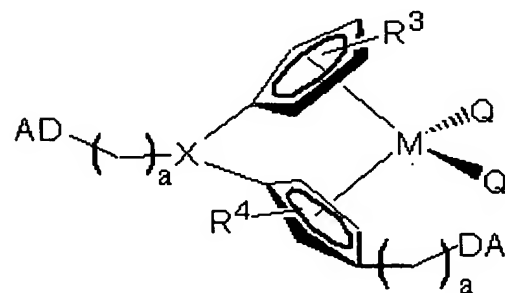
to Claim 7, wherein the first metallocene compound is one of the following compounds:



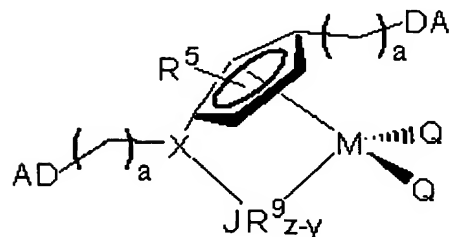
wherein each a is an integer of 4 to 8, and each A is methoxymethyl, t -butoxymethyl, tetrahydropyranyl, tetrahydrofuryl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or t -butyl.

11. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the second metallocene compound is a compound represented by the following Chemical Formula 2 or Chemical Formula 3:

Chemical Formula 2



Chemical Formula 3



wherein:

M is a group IV transition metal;

each of (C_5R^3) , (C_5R^4) and (C_5R^5) is a cyclopentadienyl which is a metalloid of a group XIV metal substituted by identical or different hydrogen radical, C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl, arylalkenyl radical or hydrocarbyl; a cyclopentadienyl wherein two neighboring carbon atoms of C_5 are connected by a hydrocarbyl radical to form one or more C_4 to C_{16} ring; or a substituted cyclopentadienyl ligand;

each Q is identical or different halogen radical; C_1 to C_{20} alkyl radical, alkenyl radical, aryl radical, alkylaryl radical, arylalkyl radical; or C_1 to C_{20} alkylidene radical;

X is a bridge that binds two cyclopentadienyl ligands or cyclopentadienyl ligands comprising a C_1 to C_4 alkylene radical, dialkyl silicon or germanium, or alkyl phosphine or amine with JR^{9-z-y} by a covalent bond;

R^9 is a hydrogen radical, a C_1 to C_{20} alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical or an arylalkyl radical;

J is a group XV element or a group XVI element;

D is an oxygen or nitrogen atom;

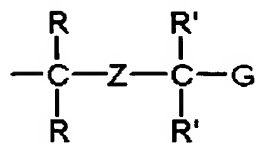
A is a hydrogen radical, a C_1 to C_{20} alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, an alkylsilyl radical, an arylsilyl radical, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl;

a is an integer of 4 to 8; and

at least one hydrogen radical of R^3 , R^4 and R^5 of (C_5R^3) , (C_5R^4) and (C_5R^5) is substituted by a radical represented by the following Chemical Formula a,

Chemical Formula b, Chemical Formula c or Chemical Formula d:

Chemical Formula a



wherein:

Z is an oxygen atom or a sulfur atom;

each of R and R' is identical or different hydrogen radical; C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl; or arylalkenyl radical; and the two R's may be connected to form a ring;

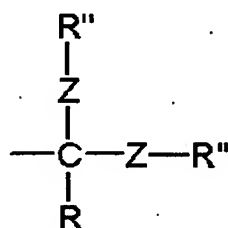
G is a C_1 to C_{40} alkoxy, aryloxy, alkylthio, arylthio, phenyl or substituted phenyl,

and may be connected to R' to form a ring;

if Z is a sulfur atom, G should be alkoxy or aryloxy; and

if G is alkylthio, arylthio, phenyl or substituted phenyl, Z should be an oxygen atom;

Chemical Formula b



wherein

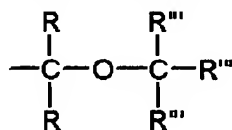
Z is an oxygen atom or a sulfur atom, and at least one of the two Zs is an oxygen atom;

each of R and R'' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

R and R'' may be connected to form a ring; and

unless both R''s are hydrogen radicals, they may be connected to form a ring;

Chemical Formula c



wherein:

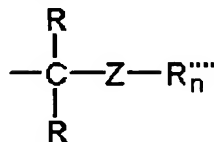
each of R and R''' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

two neighboring R'''s may be connected to form a ring; and

if at least one of Rs is a hydrogen radical, all R'''s are not hydrogen radicals, and

if at least one of R'''s is a hydrogen radical, all Rs are not hydrogen radical; and

Chemical Formula d



wherein:

Z is an oxygen, sulfur, nitrogen, phosphorus or arsenic atom;

each of R is identical or different hydrogen radical, C₁ to C₄₀ alkyl, cycloalkyl,

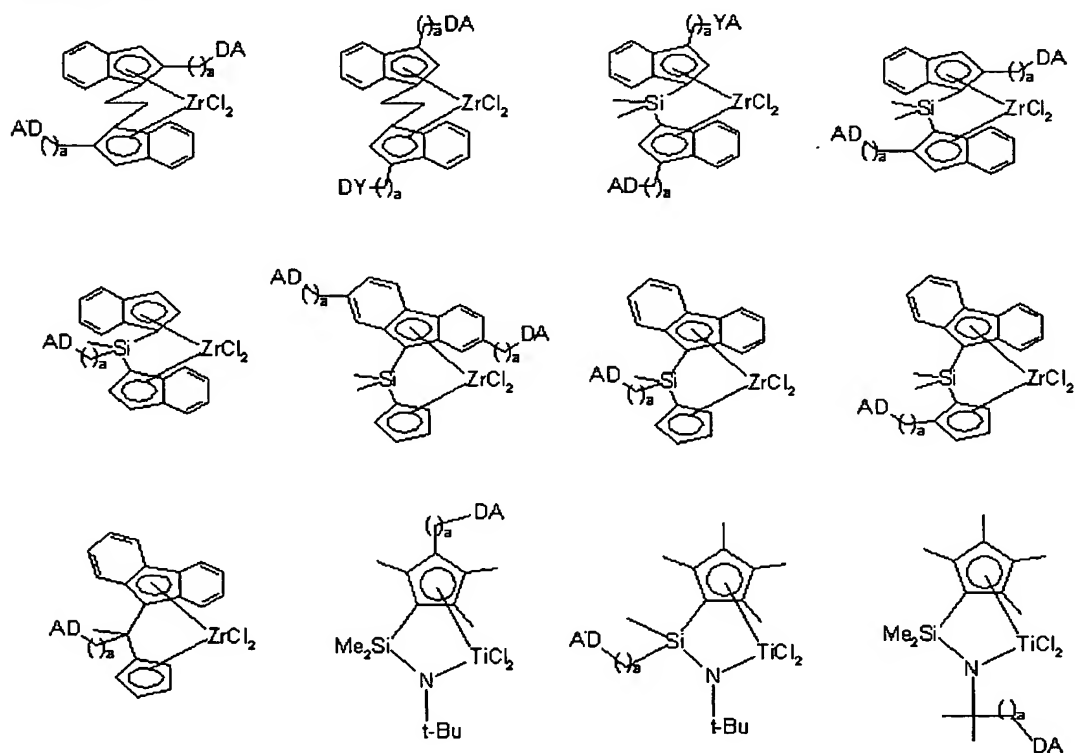
aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

R''' is a hydrogen radical or C₁ to C₄₀ alkyl, aryl, alkenyl, alkylaryl, alkylsilyl, arylsilyl, phenyl or substituted phenyl; and

n is 1 or 2, where if Z is oxygen or sulfur n is 1, and if Z is nitrogen, phosphorus or arsenic n is 2.

12. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the second metallocene compound is $[(A-D-(CH_2)_a)(CH_3)_4X(C_5H_4)(9-C_{13}H_9)]ZrCl_2$ or $[(A-D-(CH_2)_a)(CH_3)_4X(C_5Me_4)(NCMe_3)]TiCl_2$ (wherein each a is an integer of 4 to 8, each X is methylene, ethylene or silicon, each D is an oxygen or nitrogen atom, and each A is hydrogen, C₁ to C₂₀ alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkylsilyl, arylsilyl, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl).

13. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the second metallocene compound is one of the following compounds:

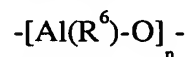


wherein each a is an integer of 4 to 8, each D is an oxygen or nitrogen atom, and each A is a hydrogen radical, a C₁ to C₂₀ alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, an alkylsilyl radical, an arylsilyl

radical, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl.

14. The supported hybrid metallocene catalyst for polymerizing preparing polyolefin according to Claim 7, wherein the cocatalyst is a compound selected from a group consisting of compounds represented by the following Chemical Formula 4, Chemical Formula 5 and Chemical Formula 6:

Chemical Formula 4



wherein:

R^6 is a C_1 to C_{20} hydrocarbyl radical substituted by identical or different halogen radical, C_1 to C_{20} hydrocarbyl radical or halogen; and

a is an integer larger than 2;

Chemical Formula 5

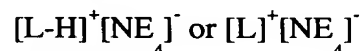


wherein:

N is aluminum or boron; and

R^7 is a C_1 to C_{20} hydrocarbyl radical substituted by identical or different halogen radical, C_1 to C_{20} hydrocarbyl radical or halogen; and

Chemical Formula 6



wherein:

L is a neutral or cationic Lewis acid;

H is a hydrogen atom;

N is a group XIII element, such as aluminum and boron; and

E is a C_6 to C_{40} aryl radical substituted by one or more C_1 to C_{20} hydrocarbyl radicals containing a halogen radical, C_1 to C_{20} hydrocarbyl, alkoxy, phenoxy radical, nitrogen, phosphorus, sulfur or oxygen atom, and the four E s may be identical or different.

15. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 14, wherein the compound represented by Chemical Formula 4 is methylaluminoxane (MAO), ethylaluminoxane, isobutylaluminoxane or butylaluminoxane.

16. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 14, wherein the compound represented by Chemical Formula 5 is trimethylaluminum, triethylaluminum, triisobutylaluminum, tripropylaluminum,

tributylaluminum, dimethylchloroaluminum, dimethylisobutylaluminum, dimethylethylaluminum, diethylchloroaluminum, triisopropylaluminum, tri-*s*-butylaluminum, tricyclopentylaluminum, tripentylaluminum, triisopentylaluminum, trihexylaluminum, ethyldimethylaluminum, methyldiethylaluminum, triphenylaluminum, tri-*p*-tolylaluminum, dimethylaluminummethoxide, dimethylaluminummethoxide, trimethylboron, triethylboron, triisobutylboron, tripropylboron or tributylboron.

17. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 14, wherein the compound represented by Chemical Formula 6 is triethylammoniumtetraphenylboron, tributylammoniumtetraphenylboron, trimethylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammoniumtetra(*p*-tolyl)boron, tripropylammoniumtetra(*p*-tolyl)boron, triethylammoniumtetra(*o,p*-dimethylphenyl)boron, trimethylammoniumtetra(*o,p*-dimethylphenyl)boron, tributylammoniumtetra(*p*-trifluoromethylphenyl)boron, trimethylammoniumtetra(*p*-trifluoromethylphenyl)boron, tributylammonium tetrapentafluorophenylboron, *N,N*-diethylaniliniumtetraphenylboron, *N,N*-diethylanilinium tetrapentafluorophenylboron, diethylammoniumtetrapentafluorophenylboron, triphenylphosphoniumtetraphenylboron, trimethylphosphoniumtetraphenylboron, triethylammoniumtetraphenylaluminum, tributylammoniumtetraphenylaluminum, trimethylammoniumtetraphenylaluminum, tripropylammoniumtetraphenylaluminum, trimethylammoniumtetra(*p*-tolyl)aluminum, tripropylammoniumtetra(*p*-tolyl)aluminum, triethylammoniumtetra(*o,p*-dimethylphenyl)aluminum, tributylammoniumtetra(*p*-trifluoromethylphenyl)aluminum, trimethylammoniumtetra(*p*-trifluoromethylphenyl)aluminum, tributylammoniumtetrapentafluorophenylaluminum, *N,N*-diethylaniliniumtetraphenylaluminum, *N,N*-diethylaniliniumtetraphenylaluminum, *N,N*-diethylaniliniumtetrapentafluorophenylaluminum, diethylammonium tetrapentafluorophenylaluminum, triphenylphosphoniumtetraphenylaluminum, trimethylphosphoniumtetraphenylaluminum, triethylammoniumtetraphenylboron, tributylammoniumtetraphenylboron, trimethylammoniumtetraphenylboron, tripropylammoniumtetraphenylboron, trimethylammoniumtetra(*p*-tolyl)boron, tripropylammoniumtetra(*p*-tolyl)boron, triethylammoniumtetra(*o,p*-dimethylphenyl)boron, trimethylammoniumtetra(*o,p*-dimethylphenyl)boron, trib-

utylammoniumtetra(*p*-trifluoromethylphenyl)boron, trimethylammoniumtetra(*p*-trifluoromethylphenyl)boron, tributylammoniumtetrapentafluorophenylboron, *N,N*-diethylaniliniumtetraphenylboron, *N,N*-diethylaniliniumtetraphenylboron, *N,N*-diethylaniliniumtetrapentafluorophenylboron, diethylammonium tetrapentafluorophenylboron, triphenylphosphoniumtetraphenylboron, triphenylcarboniumtetraphenylboron, triphenylcarboniumtetraphenylaluminum, triphenylcarboniumtetra(*p*-trifluoromethylphenyl)boron or triphenylcarbonium tetrapentafluorophenylboron.

18. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the support is dried at high temperature ranging from 300 to 1,000 °C and has highly reactive siloxane groups on the surface.

19. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the support is silica, silica-alumina or silica-magnesia.

20. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the support has 0.1 to 1 mmol/g of alcohol groups (-OH) on the surface.

21. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 20, wherein the support has 0.1 to 0.5 mmol/g of alcohol groups (-OH) on the surface.

22. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the supporting amount of the first metallocene compound and the second metallocene compound is 0.1 to 20 wt% of the total supported hybrid metallocene catalyst weight, based on the weight of group IV metals comprised in each compound.

23. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the supporting amount of the cocatalyst is 1 to 10,000 mol of the group XIII metal for 1 mol of the group IV metal comprised in the second metallocene compound.

24. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, wherein the supporting amount of the second metallocene compound is 0.01 to 100 mol for 1 mol of the first metallocene compound.

25. The supported hybrid metallocene catalyst for preparing polyolefin according to Claim 7, which has been pre-polymerized by contact with an olefinic monomer.

26. A method for preparing a supported hybrid metallocene catalyst wherein at

least two different metallocene compounds are supported on a single support, which comprises:

- a) a step of contacting a supported metallocene catalyst in which at least one metallocene compound is supported with a cocatalyst to prepare an activated supported metallocene catalyst; and
- b) a step of supporting at least one metallocene compound different from the metallocene compound of the step a) on the activated supported metallocene catalyst.

27. A method for preparing a supported hybrid metallocene catalyst wherein at least two different metallocene compounds are supported on a single support, which comprises:

- a) a step of contacting at least one metallocene compound with a cocatalyst to prepare an activated metallocene compound; and
- b) a step of supporting the activated supported metallocene compound on a supported metallocene catalyst in which at least one metallocene compound different from the metallocene compound of the step a) is supported.

28. A method for preparing a supported hybrid metallocene catalyst for preparing polyolefin having a bimodal or broad molecular weight distribution, which comprises:

- a) a step of preparing a first supported catalyst by supporting a first metallocene compound having an acetal, ketal, tertiary alkoxyalkyl, benzyloxyalkyl, substituted benzyloxyalkyl, monothioacetal or monothioketal functional group on a support having siloxane groups on the surface;
- b) a step of preparing an activated first supported catalyst by contacting the first supported catalyst with an organometallic compound cocatalyst containing a group XIII metal; and
- c) a step of supporting a second metallocene compound having a bridge linkage containing at least one Lewis base in cyclopentadiene, a cyclopentadiene derivative or a bridge group on the activated first supported catalyst to prepare a supported hybrid metallocene catalyst wherein the first metallocene compound and the second metallocene compound are supported.

29. A method for preparing a supported hybrid metallocene catalyst for preparing polyolefin having a bimodal or broad molecular weight distribution, which comprises:

- a) a step of supporting a first metallocene compound having an acetal, ketal,

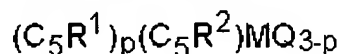
tertiary alkoxyalkyl, benzyloxyalkyl, substituted benzyloxyalkyl, monothioacetal or monothioacetal functional group on a support having siloxane groups on the surface to prepare a first supported catalyst;

b) a step of contacting a second metallocene compound having a bridge linkage containing at least one Lewis base in cyclopentadiene, a cyclopentadiene derivative or a bridge group with an organometallic compound cocatalyst containing a group XIII metal to prepare an activated second metallocene compound; and

c) a step of supporting the activated second metallocene compound on the first supported catalyst to prepare a supported hybrid metallocene catalyst wherein the first metallocene compound and the second metallocene compound are supported.

30. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the first metallocene compound is a compound represented by the following Chemical Formula 1:

Chemical Formula 1



wherein:

M is a group IV transition metal;

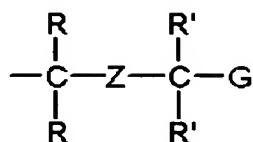
each of (C_5R^1) and (C_5R^2) is cyclopentadienyl which is a metallocene of a group XIV metal substituted by identical or different hydrogen radical, C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl, arylalkenyl radical or hydrocarbyl; cyclopentadienyl wherein two neighboring carbon atoms of C_5 are connected by a hydrocarbyl radical to form one or more C_4 to C_{16} rings; or a substituted cyclopentadienyl ligand;

Q is a halogen radical; a C_1 to C_{20} alkyl radical, alkenyl radical, aryl radical, alkylaryl radical, arylalkyl radical; or a C_1 to C_{20} alkylidene radical;

P is 0 or 1; and

at least one hydrogen radical in R^1 and R^2 is substituted by a radical represented by the following Chemical Formula a, a radical represented by the following Chemical Formula b, or a radical represented by the following Chemical Formula c:

Chemical Formula a



wherein:

Z is an oxygen atom or a sulfur atom;

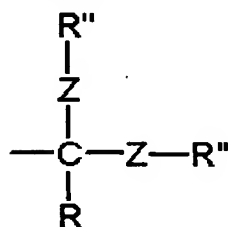
each of R and R' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl; or arylalkenyl radical; and the two R's may be connected to form a ring;

G is a C₁ to C₄₀ alkoxy, aryloxy, alkylthio, arylthio, phenyl or substituted phenyl, and may be connected to R' to form a ring;

if Z is a sulfur atom, G should be alkoxy or aryloxy; and

if G is alkylthio, arylthio, phenyl or substituted phenyl, Z should be an oxygen atom;

Chemical Formula b



wherein

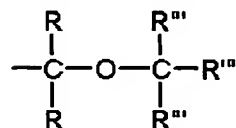
Z is an oxygen atom or a sulfur atom, and at least one of the two Zs is an oxygen atom;

each of R and R'' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

R and R'' may be connected to form a ring; and

unless both R's are hydrogen radicals, they may be connected to form a ring; and

Chemical Formula c



wherein:

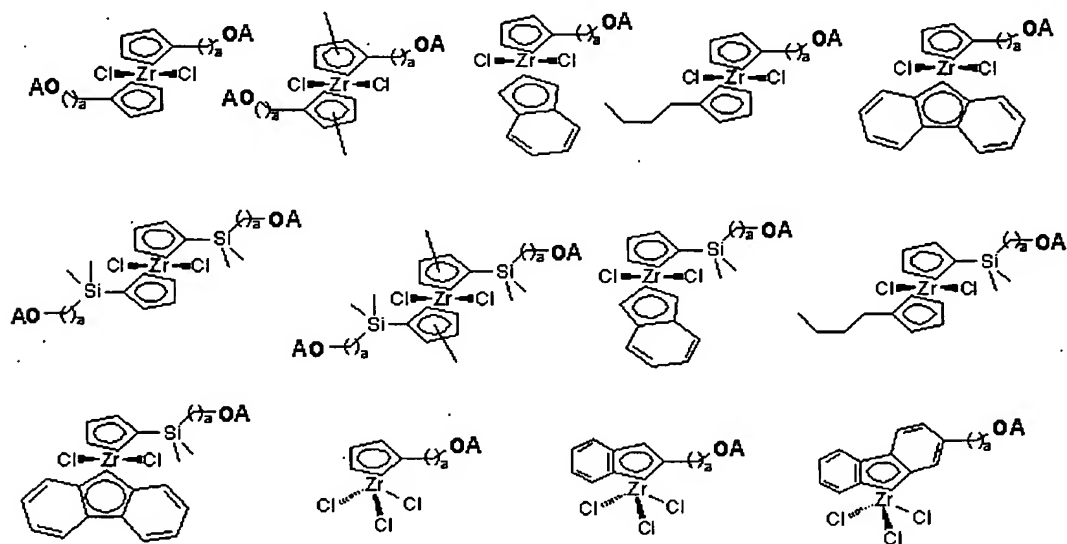
each of R and R''' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

two neighboring R'''s may be connected to form a ring; and

if at least one of Rs is a hydrogen radical, all R'''s are not hydrogen radicals, and if at least one of R'''s is a hydrogen radical, all Rs are not hydrogen radical.

31. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the first metallocene compound is $[A-O-(CH_2)_a-C(H)_2]_2ZrCl_2$ or $[A-O-(CH_2)_a-C(H)_2]_3ZrCl_3$ (wherein each a is an integer of 4 to 8, and each A is methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuryl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl).

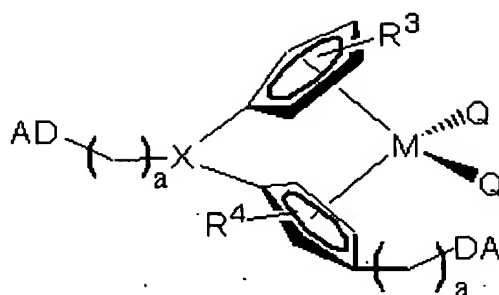
32. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the first metallocene compound is one of the following compounds:



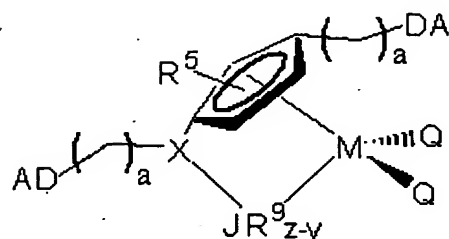
wherein each a is an integer of 4 to 8, and each A is methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuryl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl.

33. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the second metallocene compound is a compound represented by the following Chemical Formula 2 or Chemical Formula 3:

Chemical Formula 2



Chemical Formula 3



wherein:

M is a group IV transition metal;

each of (C_5R^3) , (C_5R^4) and (C_5R^5) is a cyclopentadienyl which is a metallocene of a group XIV metal substituted by identical or different hydrogen radical, C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl, arylalkenyl radical or hydrocarbyl; a cyclopentadienyl wherein two neighboring carbon atoms of C_5 are connected by a hydrocarbyl radical to form one or more C_4 to C_{16} ring; or a substituted cyclopentadienyl ligand;

each Q is identical or different halogen radical; C_1 to C_{20} alkyl radical, alkenyl radical, aryl radical, alkylaryl radical, arylalkyl radical; or C_1 to C_{20} alkylidene radical;

X is a bridge that binds two cyclopentadienyl ligands or cyclopentadienyl ligands comprising a C_1 to C_4 alkylene radical, dialkyl silicon or germanium, or alkyl phosphine or amine with JR^9 by a covalent bond;

R^9 is a hydrogen radical, a C_1 to C_{20} alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical or an arylalkyl radical;

J is a group XV element or a group XVI element;

D is an oxygen or nitrogen atom;

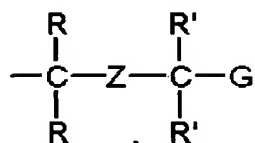
A is a hydrogen radical, a C_1 to C_{20} alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, an alkylsilyl radical, an arylsilyl radical, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl;

a is an integer of 4 to 8; and

at least one hydrogen radical of R^3 , R^4 and R^5 of (C_5R^3) , (C_5R^4) and (C_5R^5) is substituted by a radical represented by the following Chemical Formula a,

Chemical Formula b, Chemical Formula c or Chemical Formula d:

Chemical Formula a



wherein:

Z is an oxygen atom or a sulfur atom;

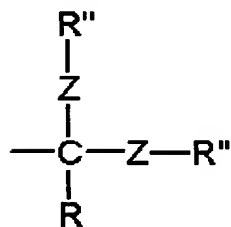
each of R and R' is identical or different hydrogen radical; C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl; or arylalkenyl radical; and the two R's may be connected to form a ring;

G is a C_1 to C_{40} alkoxy, aryloxy, alkylthio, arylthio, phenyl or substituted phenyl, and may be connected to R' to form a ring;

if Z is a sulfur atom, G should be alkoxy or aryloxy; and

if G is alkylthio, arylthio, phenyl or substituted phenyl, Z should be an oxygen atom;

Chemical Formula b



wherein

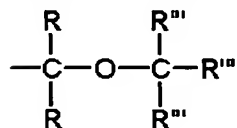
Z is an oxygen atom or a sulfur atom, and at least one of the two Zs is an oxygen atom;

each of R and R'' is identical or different hydrogen radical; C_1 to C_{40} alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

R and R'' may be connected to form a ring; and

unless both R''s are hydrogen radicals, they may be connected to form a ring;

Chemical Formula c



wherein:

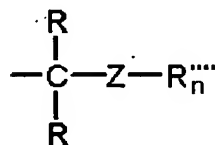
each of R and R''' is identical or different hydrogen radical; C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

two neighboring R'''s may be connected to form a ring; and

if at least one of Rs is a hydrogen radical, all R'''s are not hydrogen radicals, and

if at least one of R'''s is a hydrogen radical, all Rs are not hydrogen radical; and

Chemical Formula d



wherein:

Z is an oxygen, sulfur, nitrogen, phosphorus or arsenic atom;

each of R is identical or different hydrogen radical, C₁ to C₄₀ alkyl, cycloalkyl, aryl, alkenyl, alkylaryl, arylalkyl or arylalkenyl radical;

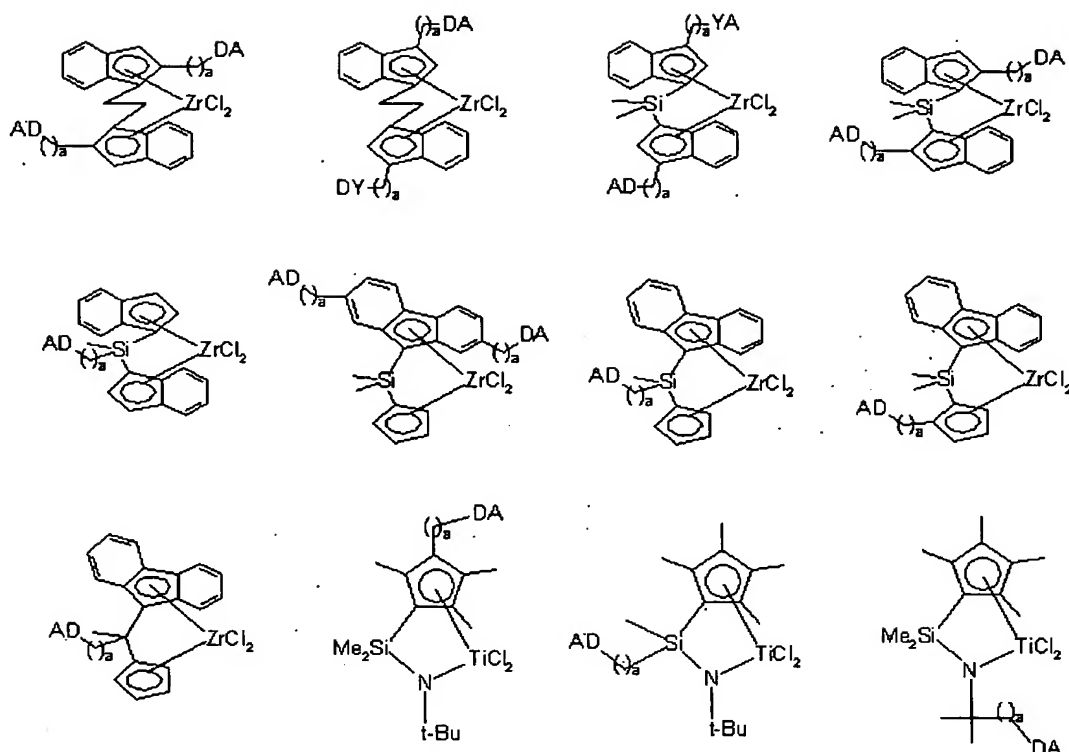
R''' is a hydrogen radical or C₁ to C₄₀ alkyl, aryl, alkenyl, alkylaryl, alkylsilyl, arylsilyl, phenyl or substituted phenyl; and

n is 1 or 2, where if Z is oxygen or sulfur n is 1, and if Z is nitrogen, phosphorus or arsenic n is 2.

34. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the second metallocene compound is

$[(A-D-(CH_2)_a)(CH_3)_3X(C_5H_4)(9-C_{13}H_9)]ZrCl_2$ or $[(A-D-(CH_2)_a)(CH_3)_3X(C_5Me_4)(NCMe_3)]TiCl_2$ (wherein each a is an integer of 4 to 8, each X is methylene, ethylene or silicon, each D is an oxygen or nitrogen atom, and each A is hydrogen, C₁ to C₂₀ alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkylsilyl, arylsilyl, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl).

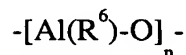
35. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the second metallocene compound is one of the following compounds:



wherein each a is an integer of 4 to 8, each D is an oxygen or nitrogen atom, and each A is a hydrogen radical, a C_1 to C_{20} alkyl radical, an alkenyl radical, an aryl radical, an alkylaryl radical, an arylalkyl radical, an alkylsilyl radical, an arylsilyl radical, methoxymethyl, *t*-butoxymethyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxyethyl, 1-methyl-1-methoxyethyl or *t*-butyl.

36. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the cocatalyst is a compound selected from a group consisting of compounds represented by the following Chemical Formula 4, Chemical Formula 5 and Chemical Formula 6:

Chemical Formula 4

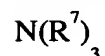


wherein:

R^6 is a C_1 to C_{20} hydrocarbyl radical substituted by identical or different halogen radical, C_1 to C_{20} hydrocarbyl radical or halogen; and

a is an integer larger than 2;

Chemical Formula 5

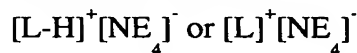


wherein:

N is aluminum or boron; and

R^7 is a C_1 to C_{20} hydrocarbyl radical substituted by identical or different halogen radical, C_1 to C_{20} hydrocarbyl radical or halogen; and

Chemical Formula 6



wherein:

L is a neutral or cationic Lewis acid;

H is a hydrogen atom;

N is a group XIII element, such as aluminum and boron; and

E is a C_6 to C_{40} aryl radical substituted by one or more C_1 to C_{20} hydrocarbyl radicals containing a halogen radical, C_1 to C_{20} hydrocarbyl, alkoxy, phenoxy radical, nitrogen, phosphorus, sulfur or oxygen atom, and the four Es may be identical or different.

37. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the support is dried at high temperature ranging from 300 to 1,000 °C and has highly reactive siloxane groups on the surface.

38. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the support is silica, silica-alumina or silica-magnesia.

39. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the support has 0.1 to 10 mmol/g of alcohol groups (-OH) on the surface.

40. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the supporting amount of the first metallocene compound and the second metallocene compound is 0.1 to 20 wt% of the total supported hybrid metallocene catalyst weight, based on the weight of group IV metals comprised in each compound.

41. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the supporting amount of the cocatalyst is 1 to 10,000 mol of the group XIII metal for 1 mol of the group IV metal comprised in the second metallocene compound.

42. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, wherein the supporting amount of the second metallocene compound is 0.01 to 100 mol for 1 mol of the first metallocene compound.

43. The method for preparing a supported hybrid metallocene catalyst according to Claim 28 or Claim 29, which further comprises a step of contacting the supported hybrid metallocene catalyst with an olefinic monomer to prepare a pre-polymerized catalyst.

44. A method for olefin polymerization comprising a step of polymerizing an olefinic monomer in the presence of a supported hybrid metallocene catalyst wherein at least two different metallocene compounds, which comprise a first metallocene compound whose ligand is supported to the support surface by chemical bonding, a second metallocene compound whose ligand is supported to a cocatalyst, which is chemically bonded to the support surface, by chemical bonding, a cocatalyst and a support, are supported on a single support.

45. The method for olefin polymerization according to Claim 44, wherein the first metallocene compound is a catalyst for low molecular weight polyolefin polymerization and the second metallocene compound is a catalyst for high molecular weight polyolefin polymerization.

46. The method for olefin polymerization according to Claim 45, wherein the low molecular weight polyolefin has a molecular weight ranging from 1,000 to 100,000, and the high molecular weight polyolefin has a molecular weight higher than that of the low molecular weight polyolefin, ranging from 10,000 to 1,000,000.

47. The method for olefin polymerization according to Claim 44, wherein the first metallocene compound is supported on the support by a chemical bond of its ligand to the support surface; and the second metallocene compound is supported on the support by a chemical bond of its ligand to a cocatalyst chemically bonded to the support surface.

48. The method for olefin polymerization according to Claim 44, wherein the supporting amount of the metallocene compounds is 0.1 to 20 wt% of the total supported hybrid metallocene catalyst weight, based on the weight of metals comprised in each metallocene compound.

49. The method for olefin polymerization according to Claim 44, wherein the supporting amount of said at least one metallocene compound is 0.01 to 100 mol for 1 mol of the other metallocene compound.

50. The method for olefin polymerization according to Claim 44, wherein a cocatalyst component for polyolefin polymerization is further supported on the supported hybrid metallocene catalyst.

51. The method for olefin polymerization according to Claim 50, wherein the supporting amount of the cocatalyst is 1 to 10,000 mol for 1 mol of metals comprised in the metallocene compound.
52. A method for preparing polyolefin having a bimodal or broad molecular weight distribution, which comprises a step of polymerizing an olefinic monomer in the presence of the supported hybrid metallocene catalyst according to Claim 7.
53. The method for preparing polyolefin according to Claim 52, wherein the supported hybrid metallocene catalyst has been pre-polymerized by contact with an olefinic monomer.
54. The method for preparing polyolefin according to Claim 52, wherein the polymerization is performed in a single reactor.
55. The method for preparing polyolefin according to Claim 52, wherein the polymerization is performed by a slurry process or a gas phase process.
56. The method for preparing polyolefin according to Claim 52, wherein the polymerization is performed at a temperature ranging from 25 to 500 °C.
57. The method for preparing polyolefin according to Claim 52, wherein the polymerization is performed at a pressure ranging from 1 to 100 Kgf/cm².
58. The method for preparing polyolefin according to Claim 52, wherein the supported hybrid metallocene catalyst is diluted in a C₅ to C₁₂ aliphatic hydrocarbon solvent, aromatic hydrocarbon solvent or hydrocarbon solvent substituted by a chlorine atom into a slurry, and then injected to an olefinic monomer
59. The method for preparing polyolefin according to Claim 52, wherein the olefinic monomer is selected from a group consisting of α -olefin, cyclic olefin, a dienic olefinic monomer and a trienic olefinic monomer.
60. The method for preparing polyolefin according to Claim 52, wherein the polyolefin has a molecular weight distribution (Mw/Mn) ranging from 3 to 50.